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PEER REVIEW

by Assoc. Prof. Reni Tomova, Ph.D. - Institute of Optical Materials and Technologies "Acad. J. Malinowski" (IOMT) – BAS

on Competition for an "Associate Professor" position at the IOMT – BAS in the professional field 4.2 "Chemical Sciences", speciality "Physical chemistry", announced in the State Gazette No. 79/ 04.10.2022г

Applicant: Daniela Bogdanova Karashanova PhD, Associate Professor at the Institute of Optical Materials and Technologies "Acad. Yordan Malinovski" - BAS.

1. General presentation of the received materials

I am assigned as a member of the Scientific Jury of the competition for the occupation of the academic position of Associate Professor (area 4: Natural sciences, mathematics and informatics, professional field 4.2: Chemical Sciences, scientific speciality: Physical chemistry announced for the needs of the Institute of Optical Materials and Technologies by order No. РД-15-716/ 01.12.2022 of the Director of IOMT.

Documents for participation have been submitted by a single candidate - Dr Daniela Bogdanova Karashanova, an associate professor at IOMT. All documents and materials meet the requirements of Art. 26(4) of the Law for the Development of Academic Staff in the Republic of Bulgaria (LDASRB) announced in IOMTs regulation and certify that Assoc. Prof. Karashanova meets the conditions for occupying the position of Professor mentioned in Art. 25(1).

- According to item 1 - Dr Georgieva has an acquired educational and scientific PhD degree (diploma 30334/06.04.2006, awarded by the Higher Attestation Commission);
- According to item 2: Holds the position of Associate Professor in the "Electron Microscopy" Laboratory at the Scientific and Technical Department of IOMT (Certificate of work experience).
- Regarding item 3: For participation in the competition, she submitted six publications equivalent to a monograph thesis in specialized scientific publications, which do not repeat those used for the acquisition of the educational and scientific PhD degree;
- According to item 4: She presented 13 other original research works (12 publications and patent No.: 112999/ dated 21.11.2022, issued by the Patent Office of the Republic of Bulgaria);
- According to item 5: With the 898 (Appendix 1) points collected by her, she exceeds the minimum national requirements under Art. 2b, 2 and 3 of ZRASRB and the

regulations of BAS and IOMT for the minimum requirements);

- According to item 6. There is no evidence of plagiarism in scientific works proven under the law.

2. A short biography of the applicant

Daniela Bogdanova Karashanova was born on 04.10.1968. She received her secondary education at the 9th French language high school Alphonse de Lamartine (1987). She graduated from the Faculty of Physics of Sofia University "St. Kliment Ohridski, in 1994. In 1996. was enrolled as a full-time doctoral student in the Central Laboratory of Photo processes "Acad. Yordan Malinovski" (CLF) BAS, where he successfully defended her thesis on "Physicochemical properties of vacuum deposited thin layers of silver sulfide: epitaxial growth and surface electrical properties" in 2006. She has a one-year specialization at the Interdisciplinary Center for Nanosciences of Marseille (2006 - 2007). From 2001 until now, she worked in the Electron Microscopy Laboratory of IOMT (former CLF) initially as a physicist, and after being PhD awarded, as an assistant professor, associate professor and current supervisor. In parallel, Assoc. Professor Karashanova held the following positions: Representative in the Program Committee of the program Horizon 2020 (configuration Nanotechnologies, Vanguard Materials, Biotechnologies, Vanguard Production and Processing) at the Ministry of Education and Culture (2014 - 2020); Member (2019 - 2021) and Deputy Chairman (2021-2021) of the permanent scientific-expert committee on Chemical Sciences at the Scientific Research Fund of the Ministry of Education and Science.

3. General characteristics of the applicant's scientific activity

Scientific activity of Assoc. Prof. Karashanova is in the field of obtaining thin layers by vapour phase deposition, obtaining fibers by the "electrospinning" method, and studying the structure of materials using the methods of Transmission Electron Microscopy (TEM) and Electron Diffraction (SAED).

Prof. Karashanova has an impressive scientific output, widely promoted at big forums and reflected in prestigious journals. She has personally presented five presentations at international and six at national conferences and has participated in another 26 oral and 67 poster presentations. The total number of her publications is 126, of independent citations - 590, and her h-index is 13. The 111 articles and the 518 citations have published after the competition for associate professor in 2011 (Web of knowledge). She is a proven scientist with enviable authority, sought for joint work by many prominent scientists and scientific organizations in their fields (Institute of Polymers, IONH, Institute of Catalysis, IFTT, Institute of Electronics and Universities: "Prof. Asen Zlatarov" - Burgas), UHT - Plovdiv, etc.). She was the supervisor of 2 projects for organizing conferences and participated in the development of 12 national projects with FNI (10 completed and two ongoings), on 2 of which she was the coordinator for IOMT. She took part in 5 international exchange projects (EBR) - 3 with Belgium and 2 with the Estonian Academy of Sciences.

4. Pedagogical Activity

Assoc. Prof. Karashanova leads a course of lectures (30 hours) and exercises (15 hours) for PhD students on the topic "Electron microscopy and electron diffraction in the

morphological and phase analysis of materials" at the BAS Training Center. She was the supervisor of three graduates: one from SU "St. Kliment Ohridski" and two from HTMU. She was the leader of the bronze medalists of the National team of students who participated in the 1st International Tournament of Young Naturalists, 29.04.2013 - 06.05.2013, Eskişehir, Turkey. Since 2008 she has been the chairman of the organizing committee of a national forum for doctoral students and young scientists: Spring seminar of PhD students and young scientists from BAS "Interdisciplinary Chemistry", which has 15 editions.

5. General characteristics of the candidate's works

To participate in the competition, Prof. Karashanova submitted 18 scientific publications, 13 in Q1, 4 in Q2, 1 in the Q3 quartile and one patent. She presented 84 citations from 13 sources.

6. Major scientific contributions

Dr Karashanova's participation in the materials presented in the competition consists of planning and executing the transmission-microscopic studies of materials and systems that differ in their nature, structure and properties, as well as in analyzing the data on their morphology, microstructure and phase composition.

Publications equivalent to a habilitation thesis

In this group of 6 publications (A1-A6), 4 in journals with quartile Q1 and 2 with Q2, published in the last two years, associate professor Karashanova examines the application of TEM in the study of the microstructure and phase composition of innovative catalytic materials with application in the production of pure hydrogen (A1), synthesis gas, phenol (A4), the neutralization of volatile organic compounds (A6) and the decomposition of formaldehyde (A5) and methanol (A3).

Scientific approaches in the evolution of such new materials are related to reducing the size of the active phase, which leads to a reduction in the amount of catalyst used and the replacement of some of the expensive active components with cheaper ones possessing competitive activity and selectivity. TEM investigation of nanoscale materials is particularly suitable due to the atomic resolution of modern devices and the possibility of diffraction modes to determine the phase composition within a nanoparticle.

According to the shape and type of the active phase, the catalysts considered in the selected publications can be conditionally divided into 2 groups: Supported metal catalysts - A1, A4 and A5 and Oxides on porous supports- A2, A3 and A6.

The first group of metal catalysts includes "gold" - cubic gold particles deposited on supports from a mechanochemically synthesized mixture of Co3O4-CeO2, pure and doped with potassium or β-aluminium oxide (A5); "copper" - representing copper nanoparticles deposited on substrates of pure and Y-doped cerium dioxide/γ-alumina obtained by impregnation (IM) or by mechanochemical mixing (MM) of the two components (A1); and "nanosized catalysts of Ni, Ru and Pt" (alone or in a combination of two metals) deposited on zeolite support (A4).

The main scientific contributions in this group of studies are as follows:

- With electron diffraction, the presence of a non-stoichiometric phase of the fluorite-type cerium oxide $Ce_{11}O_{20}$ on the Co_3O_4-CeO_2 substrate, pure or containing a potassium additive has been proven. This phase has oxygen vacancies like CeO_2, where the gold nanoparticles are deposited. On the support containing β-Al2O_3, the gold nanoparticles preferentially deposited on the aluminium oxide and near the aluminium oxyhydroxide, thanks to the hydroxyl groups that serve as ligands for their attachment A5.

- A difference in the phase composition and structure of a copper catalyst deposited on a Y-doped cerium/alumina support has been found depending on the preparation method (impregnation (IM) or mechanochemical mixing (MM), which explains the different behavior of the catalyst in the displaced water vapor–gas reaction. It has proved that separate phases of Y_2O_3 and CeO_2 simultaneity present on the substrate at MM. At IM the cerium phase covers Al_2O_3 and forms a complex multicomponent ($Al_{10}Ce_{0.02}O_{24}Y_{5.98}$) phase, limiting the interaction between CuO and CeO2, lowers the catalytic activity of the IM catalyst A1.

- Zeolite particles used as support for nanosized catalysts of Ni, Ru and Pt in a reaction for demethoxylation and dealkylation of propyl phenol were visualized and characterized as "beta" type by TEM. The particles of the active phase, located on the zeolite surface, have been established with electron diffraction.

The second group of catalysts considers oxide multicomponent systems with several different phases supported on different porous supports: a mixture of Co-Mn oxides on macro-mesoporous silica (MMS) **A2** support, mixed Mn-Ce oxides synthesized directly on mesoporous amorphous silicon dioxide (SBA-15) **A6** as well as mixed Co-Zn ferrites deposited on modified carbon foam **A3**. Information about the structure of the substrates, the phase composition of the active components and their distribution on the surface, related to the catalytic activity in the reactions of complete oxidation of CO and n-hexane in **A2**, removal of volatile organic compounds in automobile exhaust in **A6** and the decomposition reaction of methanol to H_2 in **A3** have extracted by TEM.

As the most significant scientific contributions in this group can be a list:

- For the first time, macro-mesoporous silica (MMS) modified separately or simultaneously with cobalt and manganese oxides was used as a catalyst carrier for oxidation reactions (in the oxidation of CO and n-hexane). The MMS sample modified only with cobalt oxide has the highest catalytic activity, and those with manganese oxide have the lowest. With TEM, it has been established that on the surface and in the pores of the carrier obtained by separate modification, agglomerates of the respective oxides were observed in the case of simultaneous modifications of mixed oxides deposited mainly in the mesopores of MMS. The latter proves that the encapsulation of the pores with mixed Co-Mn oxides is responsible for the lower catalytic activity of the co-modified catalyst A2.

- With TEM and EDS, it has been proven that Mn-Ce oxides are uniformly dispersed both on the surface and perpendicularly and longitudinally in the pores of the SBA-15 carrier. With Fourier transformation, the presence of a phase of MnO2 has been established at molar ratios Mn: Ce, 2:1 and 1:2, which proves the presence of Mn4+ significantly, increases the activity of the catalyst in the reaction of propane oxidation A6.

- The highest degree of methanol conversion (over 90% at 670 – 690 °C) has been achieved with a pure cobalt ferrite catalyst supported on carbon foam supports, synthesized with 40 and 60 wt% furfural A3.

Publications outside the habilitation thesis

Outside the thesis, 12 publications (8 in quartile Q1, 3 in Q2 and 1 in Q3) and one patent, examining the application of Transmission Electron Microscopy in the study of graphene and thin-film materials B1-B6 (Topic 2) and metal and composite nanoparticles obtained by laser ablation in different media B7-B12 (Topic3) are presented.

Topic 2 Transmission electron microscopy of graphene and thin-film materials

Graphene, with its unique physical properties – zero band gap and lack of absorption, is considered one of the materials of the future in the field of electronics and optoelectronics.

Three of the papers are devoted to the deposition and investigation of classical thin films of bilayer graphene (B1), microcrystalline carbon films (B2) and carbon-doped titanium oxide (B5). The layers obtained by chemical vapour deposition (B1), laser ablation (B2) and magnetron sputtering (B5) on copper foil (B1), SiO2/Si (B2) and glass (B5) substrates. The remaining three, B3, B4 and B6, refer to liquid-suspended graphene and graphene-like flakes obtained by pulsed laser ablation of a graphite target with an Nd: YAG laser at the fundamental (1064 nm), second (532 nm) and fourth harmonic (266 nm) wavelength.

Undoubtedly, the contributions in this group of materials are many, but the following are the main ones:

- The possibility for chemical vapour deposition of double-layer graphene from graphite target has been proven, and the angle of rotation of the deposited planes was determined (B1).

- It is found that films obtained by laser ablation of graphite targets have a mixed morphology. Up to 1 nm, the graphene particles are oriented parallel to the surface of the substrate, up to several nanometers - perpendicular, and after 20 – 30 nm they form aggregates of polycrystalline graphite (B2).

- The morphology and phase composition of highly carbon-doped TiO2 layers obtained by simultaneous magnetron sputtering from two targets were characterized by TEM. The presence of 2 crystalline phases of TiO2 (anatase and rutile) and one mixed with composition: Ti3C20O14 have been found. The phase composition of the layers does not change during annealing (B5).

- The method of laser ablation from a graphite target in liquid is easy to use, effective for obtaining stable suspensions of graphene and graphene-like materials, and applicable for functionalizing graphene surfaces (B3, B4, B6).

Topic 3 Transmission Electron Microscopy of Metal and Composite Nanoparticles Produced by Laser Ablation in Different Media

Metal nanoparticles exhibit remarkable electronic, optical, magnetic and catalytic properties, which make them the object of increased and unabated research interest in recent years. These properties allow their application in various devices and advanced technologies, some of which are in the fields of biomedical engineering, pharmacy, energy storage, light technologies and environmental protection.

This section includes articles dealing with the use of TEM in the analysis of a wide range of materials obtained by pulsed laser ablation of metals (B7, B10, B12), combinations of metals (B11) and combinations of metals and oxide compounds too (B8, B9). The materials were synthesized in a vacuum (B8, B9), in the air (B11) and liquids of doubly distilled water (B10, B12) and ethanol (B10).

Fundamental contributions to this topic include:

- The presence of cubic Ag nanoparticles in a suspension obtained by pulsed laser ablation with Nd: YAG on an Ag target immersed in doubly distilled water was proven. It has been found that the size of the particles decreases with an increasing wavelength of the incident laser light and increases with increasing energy density (B7).

- There were visualized and characterized Silver and gold nanoparticles in a SiO2 matrix. It was found that in laser-annealed composites, the particle size significantly increased under the influence of the introduced beam energy, in contrast to the particle size in thermally annealed composites, which did not change (B8).

- Silver and gold nanoparticles in a SiO2 matrix were visualized and characterized. It was found that in the laser-heated composites, the size of the particles significantly increases under the influence of the energy introduced by the beam, while the thermally annealed does not change in the (B8).

- A composite of ZnO with ion-implanted AgNPs, finding application as a material for surface-enhanced Raman scattering, was successfully synthesized. The TEM results show that the silver nanoparticles distributed in the ZnO matrix in a manner dependent on the parameters of the laser radiation used in the post-annealing procedure of the composite (B9).

- It has been established that upon ablation of magnetic materials, in the presence of an external magnetic field, in a gaseous or liquid medium on a substrate, chains of nanoparticles parallel to the magnetic field are formed. The preparation of a composite with oriented nanowires of Ni, NiO (B10) and magnetite (B11), partially covered with spherical silver nanoparticles magnetite (B11) visualized. It has shown

that the length of the chains formed in ethanol is ten times shorter than those obtained in water due to the lower efficiency of the ablative process and that increasing the Ag content in the nanocomposite worsens the degree of orientation of the nanowires.

- The parameters of fine-tuning the laser radiation to reduce the average size of the silver particles below the limit of 10 nm for their ophthalmic application have been established. (B12, C1).

7. Author's contribution to the articles presented in the competition

The works presented by the candidate are collective works, including several authors. Nevertheless, taking into account the thoroughly considered, impeccably structured and well-formulated contributions, as well as my excellent personal impressions of her work, I vigorously believe that Prof. Karashtanova made a significant contribution to the planning of the experiments, obtaining and interpreting the results related to TEM and SAED, as well as in shaping the publications in this part thereof. I have no critical remarks or recommendations for the applicant

CONCLUSION

The documents and materials submitted by Assoc. prof. Daniela Bogdanova Karashanova meets all the requirements of the Regulations for the Application of the Law on the Development of the Academic Staff in the Republic of Bulgaria (ZRASRB), as well as the Regulations for the Application of the ZRASRB in BAS IOMT.

The applicant has submitted a sufficient number of scientific works published after the materials used to acquire the academic position Of Associate Professor. The evidentiary material corresponds to 898 points, which exceeds 1,5 times the minimum requirements for occupying the academic position of Professor of the BAS and 1,4 times the minimum requirements of the IOMT. In the presented results, there are enough scientific contributions to guarantee its successful future development in Electron and Transmission Microscopy and Electron Diffraction.

All this gives me the reason to share my positive assessment and to recommend to the Scientific Jury to prepare a report-proposal to the IOMT Scientific Council for the election of Assoc. Prof. Daniela Bogdanova Karashanova to the academic position of Professor" in area 4. Natural Sciences, professional direction 4.2. Chemical sciences, scientific speciality "Physicochemistry".

Sofia, 27.01.2023

Reviewer: .....

Assoc. Prof. Dr. Reni Tomova